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The first direct measurement of the fluorine-atom ground state fine structure transition, using diode laser absorption spectroscopy, is reported. The fine structure absorption line position (spin-orbit energy splitting), measured with high precision relative to a pure rotational transition in H_2O, is 404.11 $cm^{-1} \pm$ 0.04. The measured radiative lifetime is 1060 sec $\pm$ 25%, and the collision-broadened linewidth in argon (full width at half maximum) is approximately 2.3 x 10^{-4} cm^{-1}/Torr (0.17 cm^{-1}/atm). Application of the

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Abstract (Continued)

diode laser absorption technique to measurement of F-atom concentrations in chemical lasers is also discussed.

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DEVELOPMENT OF A DIODE LASER FLUORINE ATOM DIAGNOSTIC

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Alan C. Stanton and Charles E. Kolb

November 1979

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DIRECT ABSORPTION MEASUREMENT OF THE FORBIDDEN
$2p\ ^2P_{3/2} - 2p\ ^2P_{1/2}$ TRANSITION IN ATOMIC FLUORINE

A.C. Stanton and C.E. Kolb

Center for Chemical and Environmental Physics
Aerodyne Research, Inc.
Bedford Research Park, Crosby Drive
Bedford, Massachusetts 01730

We report the first direct measurement of the fluorine-atom ground state fine structure transition, using diode laser absorption spectroscopy. The $^2P_{3/2} - {}^2P_{1/2}$ absorption line position (spin-orbit energy splitting), measured with high precision relative to a pure rotational transition in H_2O, is $404.11\ cm^{-1} \pm 0.04$. The measured radiative lifetime is 1060 sec ($\pm$ 25%), and the collision-broadened linewidth in argon (full width at half maximum) is approximately $2.3 \times 10^{-4}\ cm^{-1}$/Torr (0.17 cm^{-1}/atm).

The ground multiplet of atomic fluorine is an inverted doublet, with $^2P_{3/2}$ and $^2P_{1/2}$ electronic states which are split by spin-orbit interaction. To date, the spin-orbit splitting in fluorine has been inferred only through indirect measurements, including differences in observed vacuum UV line positions,[1-3] and a recent measurement of the Raman shift frequency for scattering from the fine structure transition.[4] The fine structure

splitting inferred from these measurements is 404 cm^{-1},[5] with an uncertainty of approximately $\pm$ 1 cm^{-1}.

In this Letter we report the first direct observation of the strongly forbidden $^2P_{3/2}$ - $^2P_{1/2}$ transition in atomic fluorine, using diode laser absorption spectroscopy. The experiments have permitted a precise determination of the fine structure energy splitting as well as a measurement of the radiative lifetime for the transition. The latter measurement is of current interest because of possible application of the diode laser absorption technique to measurement of F-atom concentrations in chemical laser systems.[6-7] In addition, the measurement provides a test of the theory[8-10] of the forbidden $^2P_{3/2}$ - $^2P_{1/2}$ transitions in the halogen atoms.

The experimental setup employs a 2450 MHz microwave discharge in F_2/Ar mixtures (using a 10.7 mm I.D. alumina discharge tube in an Evenson-type cavity[11]) as the source of fluorine atoms. This source produces fractional dissociation of F_2 in excess of 70% at low F_2 flow rates (static pressure $\leq$ 10 Torr). In the present experiment, the discharge is operated at higher pressures ($\sim$ 32 Torr) in order to ensure collisional relaxation of the nonthermal $^2P_{1/2}$ - $^2P_{3/2}$ population ratio which is produced in the discharge. For these conditions the fractional dissociation is limited by the available microwave power (100 W) to approximately 15%.

The experimental arrangement is shown in Fig. 1. The discharged gas mixture, containing Ar, F_2, and F, is expanded into a 10 cm I.D. flow tube which is pumped by a Kinney KMBO 1602 vacuum system, with an effective pumping speed of approximately 1000 cfm. The pumps are protected by a
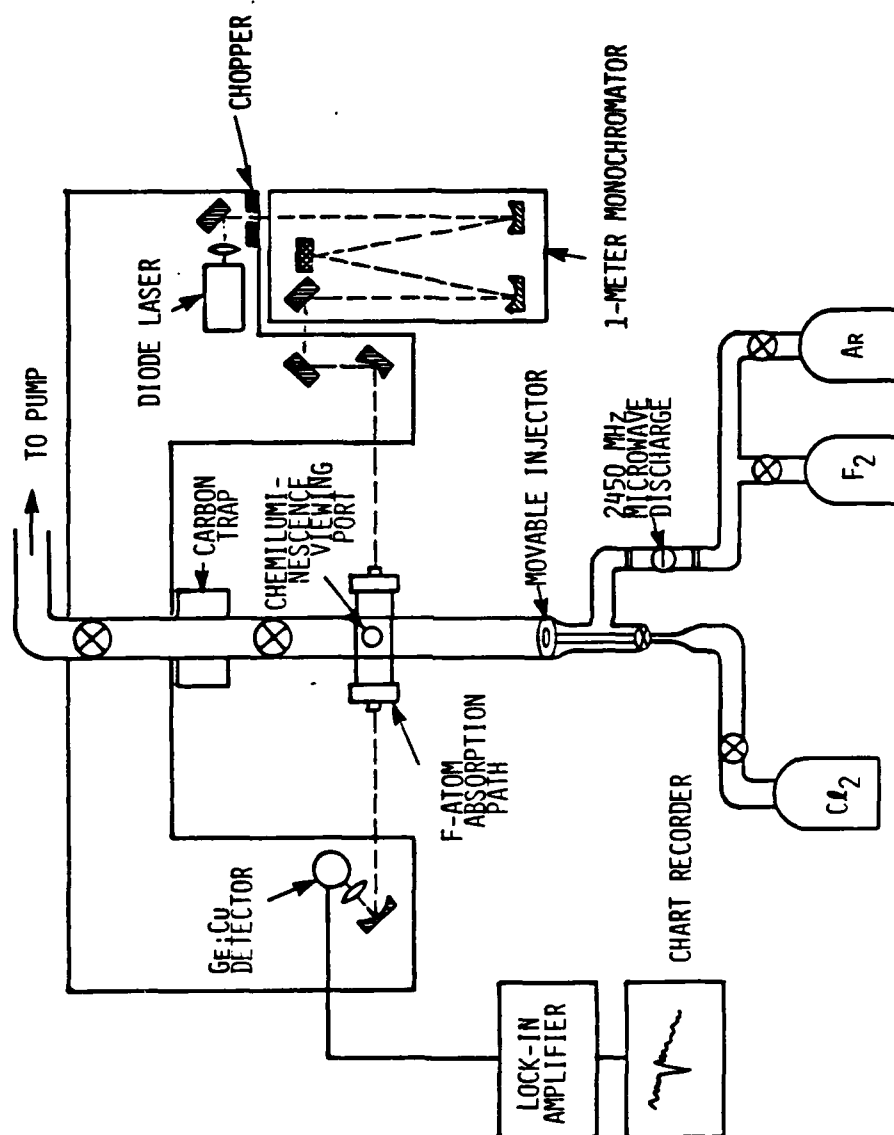
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Figure 1. Experimental Arrangement for Measurement of the $^2P_{3/2} - {}^2P_{1/2}$ F-Atom Transition

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carbon trap, which chemically removes the fluorine. The infrared absorption measurement is made transverse to the flow, with a 10 cm absorption path length. The F-atom concentration in the measurement region is typically on the order of 10^{15} cm^{-3}. Parallel KRS-5 windows mounted on sidewall ports provide optical access in the far infrared for the absorption measurement.

The laser source used in the experiment is a tunable lead-salt semi-conductor laser supplied by Laser Analytics, Inc. Diode lasers typically emit several modes, separated by $1 - 2$ cm^{-1}. A 1-meter monochromator, equipped with a 30 groove/mm grating blazed for 30 µm, is used in the present experiment to select a single mode, which is tunable across the spectral bandpass of the monochromator by variation of the current supplied to the laser. The monochromator was calibrated with a helium-neon laser dispersed in very high orders of the grating, and by scanning the pure rotational absorption spectrum of H_2O from 390 cm^{-1} to 420 cm^{-1} using a globar source. For operation near 404 cm^{-1}, the diode laser used in this experiment emitted a single mode which was tunable from 403.4 cm^{-1} to 404.7 cm^{-1}, with a frequency tuning rate of 2.6×10^{-3} cm^{-1}/mA. The laser power at the mono-chromator exit slit was approximately 10 µW, and the probe beam intensity in the F-atom absorption path (12 mm diameter collimated beam) was approximately 6 µW/cm^2. At these low intensity levels the F atom transition is completely unsaturated.

A liquid-helium cooled copper-doped germanium photoconductive detector was used to detect the transmitted laser signal. A synchronous detection scheme employing a mechanical chopper and lock-in amplifier was used to record the direct transmission spectrum. The derivative spectrum was

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generated by synchronous detection of the laser signal using a high-frequency
sawtooth modulation of the diode laser current, with the amplitude of the
current modulation chosen to provide a laser frequency variation comparable
to the linewidth of the desired absorption line. For detection of the direct
transmission spectrum, the signal-to-noise ratio was approximately 1000:1.
In both modes of operation, the laser was continuously current tuned at a
rate of 0.1 mA/s $(2.6 \times 10^{-4}$ cm^{-1}/s).

The fluorine atom concentration in the measurement region was independ-
ently measured by chemiluminescent titration with Cl_2. This technique has
been used in several previous studies,[12,13] and it has been analyzed in
detail by Nordine and Rosner.[13] The titration is based on the rapid
bimolecular reaction of F with Cl_2 to produce Cl atoms:

$$F + Cl_2 \xrightarrow{\ k_1\ } ClF + Cl \quad ,$$
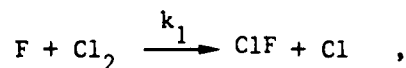
$\left[k_1 \ (300 \text{ K}) = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \right].$[14] The Cl atom production is
monitored by measurement of the afterglow intensity from the slow three-body
radiative recombination of Cl. At the titration endpoint, the Cl_2 and F atom
flow rates are equal, and further addition of Cl_2 results in no further
increase in Cl atom concentration or recombination intensity. (Reaction of
Cl with F_2 to produce ClF and F is negligibly slow for the flow conditions
used.) Corrections to the apparent endpoint to account for homogeneous
recombination of Cl atoms between the titrant injection region and the
chemiluminescence measurement region are discussed in Ref. (13). In the

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present experiment these corrections are negligible, and the accuracy of the F atom concentration inferred from the titration is determined by the accuracy of the flow rate measurements.

For the titration, the Cl_2 was injected into the 10 cm flow tube through a movable loop injector. The Cl atom recombination radiation was monitored approximately 20 cm downstream of the injector, in the region coinciding with the absorption path for the diode laser experiment. A Hamamatsu R955 phototube was mounted 90° to the absorption measurement axis, with a field-of-view which included the entire absorption path length. A filter with a sharp transmission cutoff below 610 nm was used in combination with the photomultiplier. Gas flow rates were measured with calibrated Matheson flowmeters, and pressures were measured with an MKS Industries capacitance manometer. Titration measurements of the F-atom concentration were made in conjunction with each absorption measurement.

An absolute frequency standard for the measurements was established by locating a pure rotational line in water vapor at 404.07 cm^{-1}.[15] The uncertainty in this line position is believed to be $\pm$ 0.02 cm^{-1},[15] however an uncertainty of $\pm$ 0.03 cm^{-1} is assumed here, to allow for a collision-induced frequency shift. For the 6-meter atmospheric absorption path length used in this experiment, the line-center absorption by the pressure-broadened H_2O transition is approximately 1.2%, for 60% relative humidity. The line center of the transition was located from the derivative spectrum, with an estimated precision of $\pm$ 0.01 cm^{-1}.

The fluorine atom transition was located by tuning the diode laser through its available tuning range near 404 cm^{-1} and recording the derivative spectrum. A strong derivative signal was observed near 404.1 cm^{-1} which disappeared when the discharge was extinguished. This signal corresponded to the absorption line evident in the transmission spectra shown in Fig. 2. No other absorption lines were found within the diode laser tuning range, apart from the broad H_2O absorption at 404.07 cm^{-1}. The absorption signal was found to disappear in the presence of the Cl_2 titrant, confirming absorption by atomic fluorine.

The fluorine atom line position was accurately established relative to the H_2O line at 404.07 cm^{-1} by measurement of the diode laser tuning rate using an etalon. The etalon used in this instance had a free spectral range of 9.19×10^{-3} cm^{-1} and was formed by the parallel KRS-5 windows on the flow cell. Using the etalon, the F-atom line location was established as $\nu_F^o = \nu_{H_2O}^o + (0.040\ cm^{-1} \pm 0.01)$. The energy difference between the $^2P_{3/2}$ and $^2P_{1/2}$ fine structure states in atomic fluorine is thus $\Delta E = 404.11\ cm^{-1} \pm 0.04$. (Determination of the F-atom line location using the calibrated monochromator without reference to the H_2O line yielded $\nu_F^o = 404.10\ cm^{-1} \pm 0.05$). The fluorine transition is within the collision broadened half linewidth (0.06 cm^{-1}[15]) of the H_2O line at atmospheric pressure.

The radiative lifetime for the transition was determined by comparison of the measured absorption with the measurement of fluorine atom concentration using the titration technique. The absorption coefficient is
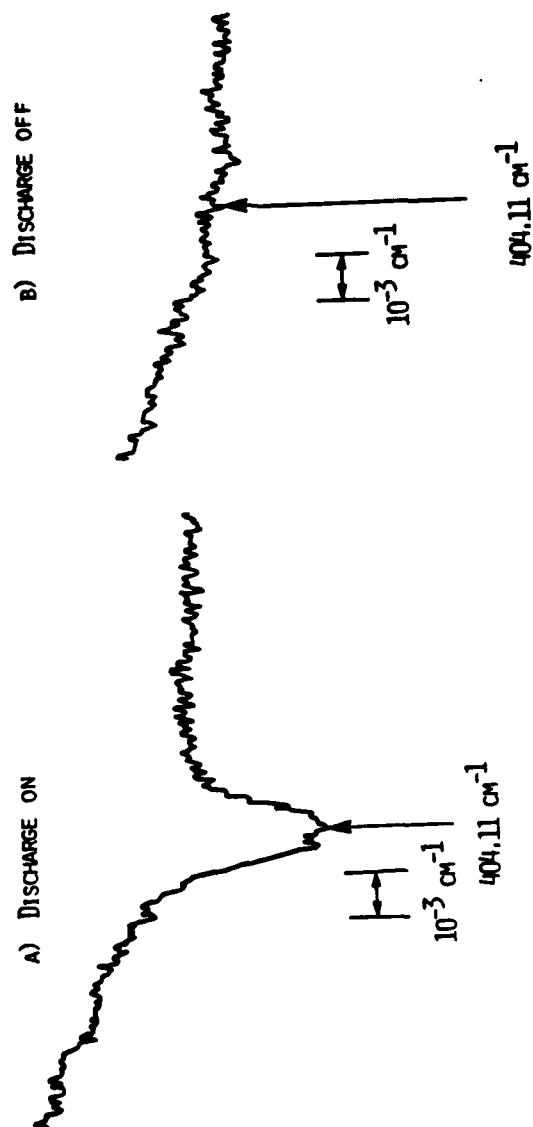
Figure 2. $^2P_{3/2} - {}^2P_{1/2}$ Absorption at 404.11 cm^{-1} in Atomic Fluorine

$$\alpha(\nu) = \frac{\lambda^2}{8\pi\tau} \left(N_{3/2} \frac{g_{1/2}}{g_{3/2}} - N_{1/2} \right) \phi(\nu) \quad , \tag{1}$$

where $N_{3/2}$ and $N_{1/2}$ are the populations of the $^2P_{3/2}$ and $^2P_{1/2}$ states, $g_{3/2}$ and $g_{1/2}$ are the degeneracies, $\phi(\nu)$ is the lineshape, and τ is the radiative lifetime. For conditions of the present experiment, a thermal population distribution at room temperature is assumed, and the quantity in parentheses in Eq. (1) becomes $N_{3/2}(g_{1/2}/g_{3/2}) - N_{1/2} = 0.40\ N_F$, where N_F is the fluorine atom concentration. (The assumption of Boltzmann equilibrium is discussed below.)

The radiative lifetime may be determined either from the measured absorption integrated over the lineshape (in which case a knowledge of the line broadening parameters is not required), or from the measured absorption at line center. The latter approach requires an accurate measurement of the linewidth in order to account for collisional broadening effects. In the present experiment, the linewidth could be accurately measured from either the derivative or direct transmission spectra, using the known diode laser tuning rate as determined from measurements using the etalon. The integrated absorption, on the other hand, was less accurately known because of poor signal to noise in the collision-broadened wings of the absorption line. The lifetime determination based on the line-center absorption was therefore generally preferred, although both techniques were used in analyzing the data. For the conditions of the experiments (4 - 10 Torr total pressure in

the measurement region) the absorption line is broadened by a combination of Doppler and collisional effects, and the lineshape at line center is

$$\phi(\nu_o) = \frac{e^{a^2} \, \text{erfc} \, (a)}{\sqrt{\pi} \, (\Delta\nu_D / 2\sqrt{\ln 2})} \qquad , \qquad (2)$$

where $\Delta\nu_D$ is the Doppler width and $a = \sqrt{\ln 2} \, \Delta\nu_C / \Delta\nu_D$ is the ratio of the collision and Dopper broadened linewidths.

The results of six experiments are presented in Table I. The collision broadened linewidths were determined by comparison of the measured linewidths with Voigt profile linewidths,[16] where the Doppler width is taken to be the calculated value of $\Delta\nu_D = 1.15 \times 10^{-3} \, \text{cm}^{-1}$ at 300 K. Assuming the collisional broadening is by argon ($p_{F_2} \leq 0.7$ Torr in all experiments), a mean broadening coefficient of $2.3 \times 10^{-4} \, \text{cm}^{-1}$/Torr Ar is obtained from the experiments.

The experimental radiative lifetimes given in Table I were obtained from the line center absorption measurements, using the mean collisional broadening coefficient in evaluating the lineshape function. The experimental uncertainty in the lifetime measurement is estimated as $\pm$ 25%, based on a 20% uncertainty in the F-atom concentrations determined from the titrations, a 15% uncertainty in the measured line center absorption coefficient, and a 10% uncertainty in the broadening coefficient. The radiative lifetime for the $^2P_{3/2} - ^2P_{1/2}$ transition, taken as the mean of the measured values, is $\tau = 1060$ s ($\pm$ 25%). This value compares favorably with a mean value of $\tau = 1240$ s obtained from the measured integrated absorption in Experiments 1, 5, and 6.

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TABLE I. Results of $^2P_{3/2} - {}^2P_{1/2}$ Absorption Experiments in Atomic Fluorine

Experiment	P, Torr	P_{Ar}, Torr	N_F, cm^{-3}	$\alpha(\nu_o)$, cm^{-1}	$\Delta\nu_C$, cm^{-1}	τ, s
1	4.17	3.75	1.37×10^{15}	1.60×10^{-3}	8.2×10^{-4}	1260
2	4.40	4.00	8.16×10^{14}	1.29×10^{-3}	8.5×10^{-4}	901
3	4.54	4.05	1.05×10^{15}	1.44×10^{-3}	8.2×10^{-4}	1032
4	4.50	4.21	9.61×10^{14}	1.14×10^{-3}	1.0×10^{-3}	1167
5	4.90	4.13	1.59×10^{15}	2.05×10^{-3}	1.1×10^{-3}	1082
6	9.22	9.45	1.49×10^{15}	1.46×10^{-3}	2.2×10^{-3}	903

The assumption of a Boltzmann population distribution at room temperature for the two fine structure states appears to be justified by comparison with previous electron resonance studies[17] of the relative populations of the two states, using microwave discharge sources. Within the discharge itself, a highly nonequilibrium population distribution may be produced, approaching the ratio of the degeneracies in the extreme case of equilibrium with the electron temperature. Collisional relaxation of the nonequilibrium distribution by diluent gas atoms downstream of the discharge is required to attain a thermal distribution. In the present experiment (for 4 - 5 Torr conditions in the measurement region), the fluorine atoms each undergo approximately 6.1×10^6 collisions with Ar atoms during transit from the discharge to the location of the absorption measurement. The ESR studies reported in Ref. (17) showed that a Boltzmann distribution is attained in fewer than 6.4×10^6 F-Ar collisions downstream of a microwave discharge in F_2/Ar mixtures. Although a slight apparent nonequilibrium had been observed in another ESR study using discharged CF_4 as the F-atom source,[18] the observed population ratio in that study is consistent with a thermal distribution at 317 k and may indicate microwave heating of the gas rather than non-equilibrium in the fine structure states.

A further indication of a fully relaxed population distribution in the present study is obtained by comparison of the integrated absorption signals from Experiments 5 and 6. In Experiment 6, the discharge conditions of Experiment 5 were maintained while additional argon was injected downstream at the entrance to the 10 cm flow tube. The added argon resulted in an

additional 2.2×10^6 F-Ar collisions prior to the absorption measurement. The integrated absorption signals for these two experiments agreed to within 5%, indicating no significant change in the $^2P_{1/2}$ to $^2P_{3/2}$ population ratio.

The measured radiative lifetime obtained in these experiments is in good agreement with the calculated value of 845 s.[10] To the authors' knowledge, the only other measurement of the radiative lifetime for the forbidden $^2P_{3/2}$ - $^2P_{1/2}$ transition in a halogen atom has been for atomic iodine,[19] where the measured value of 0.17 s $\pm$ 0.04 is in reasonable agreement with the calculated values of 0.13 s[20] and 0.11 s.[21] The calculated lifetimes are based on a formulation for magnetic dipole transitions which was developed by Shortley.[8] This formulation, in LS-coupling, is independent of the radial part of the wave functions and an explicit result is obtained which depends only on ν^3, where ν is the transition frequency. The calculation is regarded as satisfactory to within 30%.[22]

A collision cross section of 96 $\overset{\circ}{A}^2$ for line broadening by argon may be inferred from the measured broadening coefficient of $\Delta\nu_c = 2.3 \times 10^{-4}$ cm^{-1}/ Torr. This cross section is nearly twice the measured line broadening cross section of 51 $\overset{\circ}{A}^2$ for $^2P_{3/2}$ F-atom ESR transitions broadened by argon.[23]

In summary, the results of this study include a direct and accurate measurement of the spin orbit splitting in atomic fluorine. The measurement is consistent with values which were previously inferred from indirect measurements. The measured radiative lifetime for the $^2P_{3/2}$ - $^2P_{1/2}$ transition

was found to be in agreement with calculated values. The measured collisional line broadening cross section for F-Ar is nearly twice the measured broadening cross section for ESR transitions and is similar to line broadening cross sections for infrared optical transitions in molecular species.

In the present work, the diode laser absorption technique was used to measure fluorine atom concentrations on the order of 10^{15} cm^{-3} in a 10-cm path. By use of multipass optics and derivative detection, a sensitivity of 10^{12} - 10^{13} cm^{-3} could easily be attained with this technique. The technique is therefore suitable for in-situ measurement of fluorine atom concentrations in pulsed or cw chemical lasers, where estimated F atom concentrations are 10^{14} - 10^{15} cm^{-3}.

SECTION 2
APPLICATION OF THE DIODE LASER ABSORPTION TECHNIQUE TO
MEASUREMENT OF F ATOM CONCENTATIONS
IN CHEMICAL LASERS

SECTION 2. APPLICATION OF THE DIODE LASER ABSORPTION
TECHNIQUE TO MEASUREMENT OF F ATOM CONCENTRATIONS
IN CHEMICAL LASERS

The diode laser absorption experiments discussed in Section 1 indicated
that the technique may be used for quantitative in-situ detection of fluorine
atom concentrations on the order of 10^{15} cm^{-3} for the 10 cm path length and
4 - 10 Torr conditions of the experiments. The line center F atom
absorption coefficient for these conditions is on the order of 0.001 -
0.002 cm^{-1}. By use of multipass optics (50 - 100 passes are reasonable in
a White cell configuration) and derivative detection techniques, a line center
absorption coefficient as low as 10^{-6} - 10^{-5} cm^{-1} ($N_F \sim 10^{12}$ - 10^{13} cm^{-3})
should be detectable with signal/noise on the order of 10.

Estimates of fluorine atom concentrations in chemical lasers are avail-
able for several pulsed and cw HF laser systems. These systems include an
atmospheric pressure flashlamp-initiated pulsed laser,[24] a 90-Torr photo-
initiated pulsed laser (using a frequency-doubled ruby laser as the photon
source),[25] a cw supersonic diffusion laser using thermal dissociation of
SF_6 for fluorine atom production,[26] and a premixed chain reaction cw laser
developed at Aerodyne Research, Inc.,[27] using supersonic premixing and
chemical initiation by the reaction

$$F_2 + NO \longrightarrow FNO + F \qquad .$$

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The relevant characteristics of these lasers are summarized in Table II, including estimates of the line center F atom absorption coefficient at 404.11 cm^{-1}. Pressure broadening, using the broadening coefficient for F-Ar measured in this study, is included in the estimates.

TABLE II. Estimated F-atom Concentrations and Line Center
Absorption for Four HF Laser Systems

Laser Type	Reference	P (Torr)	N_F, cm^{-3}	$\alpha(\nu_o)$, cm^{-1}
Pulsed/flashlamp initiation	(21)	840	4.8×10^{15}	4.9×10^{-5}
Pulsed/photo (laser) initiation	(22)	90	1.5×10^{15}	1.4×10^{-4}
cw diffusion/thermal initiation	(23)	10	2.8×10^{15}	2.1×10^{-3}
cw premixed/chemical initiation	(24)	24	$2\text{-}9 \times 10^{14}$	7.1×10^{-5} – 3.2×10^{-4}

The estimated line center absorption coefficient for each of these systems can be accurately measured using the spin-orbit absorption technique. The technique thus seems well suited for in-situ diagnostics of F atom concentrations in operating HF laser systems. Particular interest would lie in measuring the F atom initiation level and spatial uniformity in pulsed laser systems and in mapping the spatial distribution of F atoms in cw laser systems. We are currently considering adaptations of the diode laser absorption technique for making such measurements.

SECTION 3
PUBLICATIONS AND PRESENTATIONS OF CONTRACT WORK

SECTION 3.   PUBLICATIONS AND PRESENTATIONS OF CONTRACT WORK

I. PUBLICATIONS - Section 1 of this report has been submitted to
Physical Review Letters for publication.

II. PRESENTATIONS - The work reported in Section 1 was presented by Dr. Kolb
as part of an invited seminar to the Analytical Chemistry
Division of the National Bureau of Standards in
Gaithersburg, Maryland on November 14, 1979. The
title of the seminar was "Applications of Tunable
Diode Lasers."

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